Effect of pH variation on the subcritical crack growth parameters of glassy matrix ceramics

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Abstract: The goals of our study were to calculate the subcritical crack growth (SCG) parameters of two veneering ceramics stored in water or Streptococcus mutans (S. mutans) biofilm and remineralizing medium, with indentation flaws. Feldspar (VM7) and leucite-reinforced (VM13) glass ceramic disks (Vita Zahnfabrik, Bad Säckingen, Germany) were made according to ISO 6872. Some specimens were indented with a Vickers diamond and the crack dimensions were measured. The specimens were fractured for a calculation of inert strength or further stored in water or submitted to pH variation, under preloading tension. Finally, the SCG parameters were calculated after the specimens were fractured under four stressing rates (MPa/s). Weibull analysis was conducted on non-indented specimens. XPS was performed as qualitative analysis. The subcritical crack of leucite ceramic did not vary with the media storage, but the glass-ceramic experienced a retarded growth after pH variation. The materials presented low Weibull modulus. Qualitative elemental analyses showed chemical modification on both ceramics. Therefore, the crack growth of leucite-reinforced ceramic was less affected by the environment pH than glass-ceramic.

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Effect of Ph Variation On The Subcritical Crack Growth Parameters of Glassy Matrix Ceramics

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Short title: *Subcritical crack growth of glass ceramics*

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ABSTRACT

Objectives: The subcritical crack growth (SCG) parameters of two veneering ceramics as a function of the presence biofilm *Streptococcus mutans* (*S. mutans*) and remineralizing medium compared to water storage only.

Methods: Feldspathic (VM7) and leucite reinforced (VM13) ceramic disks (Vita Zahnfabrik, Bad Säckingen, Germany) were fabricated according to ISO 6872. Specimens were indented with a Vickers diamond and the crack dimensions were measured. The specimens were fractured for a calculation of inert strength or further stored in water or *S. mutans* biofilm and remineralizing solution for 28 days, under pre-loading tension. SCG parameters were calculated after the specimens were fractured under four stressing rates (MPa/s). Weibull analysis was conducted on non-indented specimens. XPS was performed as qualitative analysis. Data were analyzed

Results: In water only, increased stressing rate from 0.1 to 100 m/s showed the coefficient of susceptibility to SCG for both ceramic types (VM7: 27.1/-1; VM13: 89.4/-0.17) whereas in the presence of *S. Mutans*/remineralizing medium VM7 (-119.3/-140.3) was less susceptible to SCG compared to VM13 (87.9/1.18). Even though less variability in strength distribution due to indentation flaws was observed, low Weibull moduli were found for VM7 (m=5) and VM13 (m=6.8). Overall, the strength plots against the stressing rate showed the tendency of stress corrosion for both ceramic types. The XPS analysis reached a depth of 3-4 nm. Specimens that were stored in *S. mutans*/remineralizing medium presented P and higher amounts of N, Na, Ca and K. For these specimens, the phases related to the binding energy of K 2p suggested the existence of KNO, KPO3 and KAlSi2O6. Such modifications were more evident in feldspathic.

Conclusion: The exposure to *S. Mutans* and the remineraliziation medium affected subcritical crack growth parameters of glass matrix ceramics tested being less for leucite reinforced ceramic.

Keywords: Ceramics, Dental Materials, Glass matrix ceramics, Subcritical crack growth, pH

1. Introduction

Fatigue is the process from which most brittle materials fail, involving the initiation and the evolution of cracks under stresses that are too low to cause rapid fracture. Dental ceramics are susceptible to subcritical crack growth (SCG), a fatigue mechanism caused by stress corrosion. [1,2]. SCG is often caused by the presence of environmental factors that can cause significant damage under load and is described by the crack growth exponent n, a material constant that varies with the environment.[3]

From the environmental perspective, temperature, pH, electrochemical potential, concentrations of species in the solute, and oxygen concentration are determinants. In particular, pH will influence the corrosion rate of glass, depending on the solution and the concentrations of solutes in it.[4]. In the oral medium, pH variations that can affect the corrosion of ceramics are due to saliva composition, diet, regurgitation, acidulated fluorides, oral appliances and dental biofilm.[5] But little is known about the effects of pH (acidic and alkaline) due to environmental species (such as microorganisms) on the subcriticial crack growth of vitreous ceramics .

More recently, it was found water and some other chemicals have the ability of reacting directly with silica glass. A strengthening effect due to water diffusion into silica glass was proposed.[6] The authors showed water penetrates the crack and diffuses into the silica glass through the crack tip and a compressive stress is developed due to volume expansion, therefore leading to a toughening effect.

Not only the environmental, but some material and mechanical factors can affect the SCG of brittle materials. From the materials side, microstructure is preponderant. As an example, the high glass content and the low content of the crystalline phase in veneering ceramics facilitate crack propagation on the surfaces under tensile stresses.[7] As for the mechanical aspect, stress loading is important. Under slower stress rates, stress corrosion leads to SCG and the critical stress for breakage is reached with lower loading. In contrast, if the stress rate is rapid, the material will fail with practically no subcritical crack growth and with higher loads.

Moreover, crack growth of a component is influenced by flaw type, size, and location, as well as by fracture toughness. In ceramics and glasses, flaws are usually found as cracks, but three-dimensional forms, such as pores, are also possible.[8] The scatter in flaw size and distribution also leads to high variability of strength data, requiring statistical methods to describe the scatter in strength and lifetime. Additionally, in strength and crack-growth studies, one can create a controllable scenario by introducing an artificial flaw, such as an indentation crack.[9,10]

Therefore, the present study aimed to investigate the subcritical crack growth of veneering ceramics using large artificial flaws in the presence of *S. mutans* biofilm followed by immersion in remineralization medium. The hypothesis of this study were that SCG would present similar behavior for leucite and glass ceramics under pH variation.

2. Materials and methods

2.1 Disc specimens

The guidelines of ISO 6872[11] were followed to produce discs of two types of veneering ceramic, namely Vita VM7 (glass frits melted in metal oxides) and Vita VM13 (feldspar frits and leucite) (VITA Zahnfabrik, Bad Säckingen, Germany). To compensate for ceramic contraction, a metallic matrix 12% larger than the final specimen was used, where the powder and modeling liquid mixture was condensed (Vita Modeling fluid, Vita) under vibration. Excess moisture was removed with a tissue. Heat treatments were performed in a porcelain furnace (Vacumat 40, Vita Zahnfabrik, Bad Säckingen, Germany). The firing schedule provided by the ceramic manufacturer was followed. In the VM7 group, the firing began at 500°C with 4 min of pre-drying and 7.27 min of temperature rise at 55°C per min for up to 910ºC, which was maintained for 1 min and 7.27 min under vacuum. The furnace chamber was opened at 600ºC. For VM13, the firing program began at 500°C and proceeded as follows: 6 min pre-drying time, 7.5 min temperature rise time at 55°C per min for up to 880ºC,

where it was maintained for 1 min and 6.4 min under vacuum. The furnace chamber was not opened until it had cooled to 600ºC. After being air-cooled, the specimens were flattened with SiC #120, 400, 600, 800, and 1200, under coolant irrigation, at 300 rpm. The specimens were not glazed.

2.2 Static fatigue and dynamic fatigue testing

For the fatigue study, 90 specimens from each ceramic were indented in a hardness tester (Tukon 2100B model, Instron, Norwood, MA, USA) with a Vickers diamond. The indentation force was 2 kgf (11 s duration), which was large enough to create an impression size and radial cracks that allowed accurate measurements without causing chipping. The indentations were made on the centers of the disc specimens, on the tensile side.

Ten discs from each ceramic were further polished with diamond paste to a 1 µm surface finish and dripped with mineral oil before the indentation. After, the crack-size measured using the parameters (c_m and c'_0) proposed by Lawn et al. (1981)[12] and Cook et al. (1982).[10] The crack dimensions represented by c_m (crack dimension at the unstable equilibrium configuration for radial cracks) and c'_0 (crack size before testing, in the equilibrium state) were measured by optical microscopy (20x augmentation). The proviso $c_m < c'_0$, necessary for application of the equations described elsewhere[12], was observed for all specimens. These specimens were immediately subjected to biaxial flexure testing in mineral oil (inert medium) and 100 MPa/s stress rate (σ'_a) for a calculation of inert strength (σ_i). The load was applied in a universal testing (Emic DL-1000, Emic, São José dos Pinhais, PR, Brazil) until fracture occurred. The parameters c_m and σ_i were used for the subsequent calculation of fatigue parameters.

The remaining 80 disc specimens were tested after 28 days' storage in water (N=40) or *S. mutans* biofilm and remineralizing medium (N=40). The latter is a microbiological model for caries[13] that simulates pH variations. The pH of the *S. mutans*-contaminated broth was ~5.6, and the pH of the remineralizing medium was ~7.0, measured by a pH meter (MP220, Mettler Toledo, Colubus, OH, USA).

Specimens were placed in sterile 10-well acrylic culture plates containing 2 mL of broth and 0.1 mL of standardized *S. mutans* suspension. The biofilm formation was performed exactly as described by Pereira et al.[14] A standard suspension of *S. mutans* (ATCC 35688) containing 10^6 cells/mL was prepared, seeded onto brain heart infusion (BHI) agar (Difco, Detroit, MI, USA), and incubated for 24 h. After incubation (37°C in a CO_2 chamber), the growth was suspended in sterile physiological solution [0.9% sodium chloride (NaCl)], and the number of cells in suspension was counted by means of a spectrophotometer (B582, Micronal, São Paulo, Brazil). The parameters used for optical density and wavelength were, respectively, 0.620 and 398 nm.

The broth used for biofilm formation was proposed by Gibbons and Nygaard.[15] It contained 20 g trypticase, 2 g NaCl, 3 g K_2HPO_4, 2 g KH_2PO_4, 1 g K_2CO_3, 120 mg $MgSO_4$, 15 mg $MnSO_4$, and 50 g $C_6H_8O_7$ dissolved in 1000 mL of distilled water. The specimens had been previously sterilized by UV light exposure for 20 min on each side. The broth was autoclaved at 121°C for 15 min. The plates were sterilized in peracetic acid solution for 30 min. The plates were sealed and incubated at 37°C for 24 h in a CO_2 chamber. The broth was changed every other day, and new broth was placed inside the wells, for 14 days.

The specimens were then placed in a remineralizing medium[16] consisting of 0.33 g KH_2PO_4, 0.34 g Na_2HPO_4, 1.27 g KCl, 0.16 g NaSCN, 0.58 g NaCl, 0.17 g $CaCl_2 \cdot H_2O$, 0.16 g NH_4Cl, 0.2 g urea, 0.03 g glucose, 0.002 g vitamin C, and 2.7 g mucin (M-1778 porcine mucin, Sigma-Aldrich Brasil Ltda. São Paulo, Brazil) in 1000 mL of distilled water, for 14 additional days.

The specimens that had been stored in water were maintained in the same plate and had the same storage time of 28 days. All of the fatigue specimens were stored and tested to fracture with adhesive tape on the compression side. After the storage period (Fig. 1), the specimens were tested under four stressing rates (n=10): 0.1, 1, 10, and 100 MPa/s. They were fractured in deionized water during the biaxial flexure experiment in a universal testing machine (Emic DL-1000, Emic, São José dos Pinhais, PR, Brazil), under controlled loading rate (the loading rates were related to the stressing rates aforementioned). The rationale

for the design involving the storage is that the tips of the growing cracks would be saturated by the storage media even though the specimens were fractured in deionized water.

The biaxial flexural strength (MPa) was then calculated by the equation $\sigma = -0.2387P(X-Y)/b^2$, where σ is the maximum tensile stress in Pascal, *P* is the total load causing fracture in Newtons, *b* is the specimen thickness at fracture origin in millimeters, and *X* and *Y* are:[11]

$$X = (1+\upsilon)\ln(r_2/r_3)^2 + [(1-\upsilon)/2](r_2/r_3)^2$$

$$Y = (1+\upsilon)[1+\ln(r_1/r_3)^2] + (1-\upsilon)(r_1/r_3)^2$$

in which:

ν is Poisson's ratio (0.25); r_1 is the radius of the support circle in mm; r_2 is the radius of the loaded area, in mm; and r_3 is the radius of the specimen, in mm.

The flexural strength (σ) at the four stressing rates ($\sigma'_a = d\sigma/dt$) was adjusted in a linear region of log σ against log σ'_a by regression analysis, as described by Cook et al. (1981) [6] and Lawn et al. [12] (1982). This regression analysis was used to calculate the apparent kinetic parameters n´ and λ´, where the line slope [1/(n´+ 1)] and the intercept [(log λ´)/(n´ + 1)] were calculated. Transformation equations were then used to obtain the true kinetic parameters n and ϑ_0, n = 1.31 n´ and $\vartheta_0 = (2.84n'^{0.162}\sigma c_m)/\lambda'$.

2.3 Inert Strength and Weibull analysis

Twenty-nine as-polished specimens from each ceramic were subjected to biaxial flexure[11] for Weibull analysis. The specimens were tested to failure (50 kgf, 1mm/min) during the biaxial flexure experiment, but in inert medium (mineral oil).

The strength data (MPa) were ranked and were plotted against the failure probability (%). The Weibull parameters m (modulus) and characteristic strength (σ0) were obtained by computational calculation (Maximum Likelihood method, Minitab 16, Minitab Inc., State College, PA, USA). A low m is related to a

broader distribution of flaws and a greater scatter in the distribution of strength values as a function of failure probability, indicating a less homogeneous material. σ0 is the failure probability at 63.2%.[17]

The indented and non-indented fractured specimens were gold sputtered and evaluated by Scanning Electron Microscopy (SEM) (Inspect S50, FEI, Hillsboro, OR, USA).

2.4 XPS analysis

X-ray Photoelectron Spectroscopy (XPS) analysis of the ceramic discs was performed on a UNI-SPECS UHV (SPECS Scientific Instruments, Sarasota, FL, USA). The pressure of the system was less than 5 x 10-7 Pa. The MgKa x-ray source used (hυ) was 1253.6 eV, and the pass energy was adjusted to 10 eV. The inelastic background of the core level spectra Al 2p, Si 2p, K 3p, Ca 2p, O 1s, Na 1s, N 1s, P 2p and C 1s was subtracted by Shirley's method. The composition of the surface region was determined by the ratio of the peak relative areas corrected by the sensitivity factors (Scofield) of the corresponding elements.

3. Results

For a confidence interval of 95%, the maximum and minimum bounds of both ceramics overlapped, indicating that there were no statistically significant differences between the two moduli.

Even though less variability in strength distribution due to indentation flaws was observed, low Weibull moduli were found for VM7 (m=5) and VM13 (m=6.8).

The SCG parameters for both ceramics are presented in the Table 1. Overall, the strength plots against the stressing rate showed the tendency of both ceramics to stress corrosion (Fig. 2).

The XPS analysis (Fig. 3) reached a depth of 3-4 nm. All specimens showed the presence of hydrocarbons (C 1s), higher for the samples that remained in the *S. mutans* and remineralizing solution, probably as a result of contamination from organic substances in the liquids. Specimens of all groups from both ceramics presented O, Si, Al, K, Ca, Na and N on the surface. Specimens that were stored in *S. mutans*/remineralizing

medium also presented P and higher amounts of N, Na, Ca and K. For these specimens, the phases related to the binding energy of K 2p suggested the existence of KNO, KPO3 and KAlSi2O6. Such modifications were more evident in VM 7 glass ceramic that is presented in Fig. 4a.

Pores of various sizes and numbers were often observed on VM7 and VM13 specimens. Also, the fracture surfaces of VM7 were smooth, whereas VM13 specimens presented a rough fracture surface. The SEM of the fractured surfaces showed median radial cracks and subsurface lateral cracks. The main fracture characteristics, present in specimens of all stressing rates, is represented by Fig. 4b.

4. Discussion

The subcritical crack growth of both ceramics differed depending on the storage media. Because VM7 is a fully amorphous silica microstructure,[18] storage in *S. mutans*/remineralizing medium made it more susceptible to chemical and mechanical influence.[19] In reality, a strengthening effect of silica glass caused by water penetration at high temperatures for relatively large surface cracks (virtually absent for submicrometer size cracks) was observed previously.[6] This is due to water that diffuses into the glass and generates a zone of swelling around the crack tip, which cannot expand due to the surrounding glass walls, generating compressive stresses. Therefore, this explains the less steep curves of stress against stressing rates observed for VM7 kept in the *S. mutans*/remineralizing medium. To the author's knowledge this is the first study to report such occurrence in dental ceramics.

With regard to the effect of "n" values on the dependence of the medium type, while no differences were observed for VM13, VM7 soaked in such media at 37 °C for several days suffered a decrease in the crack velocity. Further research is necessary to elucidate the subcritical crack growth behavior of glass ceramics in simulated oral environments other than water. In spite of that, the "n" values found for VM7 in water agree well with the findings of other studies.[20,21]

In contrast, the stress corrosion parameter “n” was positively influenced on VM13 because of the presence of leucite in its microstructure. Della Bona[22] stated that adequate size of the crystal increases fracture toughness, improves resistance to crack propagation and, consequently, the susceptibility to subcritical crack growth. This means that VM13 is probably less susceptible to fatigue than is VM7, which has important implications for the service life of a restoration made of these materials.

The low Weibull modulus of both ceramics reflected a large scatter in defect distribution, and thus in strength. The ceramics presented the same processing technique, but VM7 was visibly more prone to the inclusion of pores than was VM13. In the present study, no differences were observed between the Weibull moduli of both ceramics. Thus, the leucite grains of VM13, which presented a rounded shape and seemed homogeneously distributed, did not affected the probability of failure of the specimens. Anyhow, the low **m** values reflect the high sensitivity to defects of these materials and limit their use for locations under low stresses. Their use in ultra-thin restrations where little-to-no preparation is required, advocated by some authors[23,24] due to their highly esthetic values, should also be seen with caution.

pH in turn, controls the rate of glass corrosion. The corrosion rate of a glass at the crack tip will occur as an exchange of alkali ions by the hydronium ions, H_3O^+, of the solution, depending on the pH.[25] Besides the increase in strength due to swelling, mobile alkali ions are also expected to cause compressive stresses around the crack, reatrading crack growth. In the present study, interactions of the remineralizing solution with the glass was evidentiated by XPS data. Therefore chemical interactions might have affected the corrosion speed in VM7. We use this information to quantify the strengthening of silica glass caused by water penetration and show that the strengthening process is most effective at high temperatures for relatively large surface cracks, but virtually absent for submicrometer size cracks.

From the SEM of the fractures, specimens at all stressing rates suffered some pre-crack growth before failure.

The method presented here for calculating the fatigue parameters is not new.[26,27] In fact, the indentation flaw method was chosen because of its main advantages: statistics are eliminated as a basis for analysis, due to data homogeneity and reproducibility; the flaw that will cause final failure is well-known; and the flaw size can be pre-determined.[28] However, a larger scatter in strength was still perceptible, which deservers further investigation. Because the residual stress after indentation contributes to augment the crack propagation force, a residual stress term was accommodated to the stress intensity through the equations to minimize its effects.[12,28,29]

5. Conclusions

From this study the following could be concluded:

1- Reliability of strength measured by Weibull moduli was more favourable for leucite reinforced ceramic than that of feldspathic ceramic.

2- The exposure to *S. Mutans* and the remineraliziation medium affected subcritical crack growth parameters of glass matrix ceramics tested being less for leucite reinforced ceramic compared to feldspathic ceramic.

Conflict of interest

The authors did not have any commercial interest in any of the materials used in this study.

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Captions to the legends and tables:

Tables:

Table 1. Fracture strength (σ) (Mpa) of VM7 and VM 13 specimens according to the stressing rates. The corresponding fatigue parameters [n/log♀0 (m/s)], inert strength (σi) (MPa) are also shown.

Figures

Fig. 1 Adapted plate with dead weights (1 kgf) used for 28-day storage in water or S. mutans/remineralizing solution. The plates also had a 3-stainless-steel-ball base as the biaxial flexure testing device. A piston touched the specimen with a 10 N dead weight.

Fig. 2 Plots of strength against the stressing rate of VM 7 (A and B) and VM 13 (C and D) kept in water and *S. mutans*/remineralizing solution, respectively. The exception was VM7 stored in *S. mutans* and remineralizing medium that had a negative "n" value (-119.37) and a complex number for log♀0. The fatigue parameters of the leucite-reinforced ceramic were higher than those of VM7, no matter the storage medium.

Fig. 3 XPS analyses of VM 7 specimens showing the peaks of the elements present on the ceramic surface of control and experimental groups.

Figs. 4a-d Acid treated (2 % HF, 20 s) glass and leucite specimens. The empty spaces suggest the crystal morphology ("honeycombs") in B. Specimens fractured at 10 MPa/s after storage in *S mutans*/remineraling medium of Glass (C) and Leucite (D) ceramics. In D, the indentation profile, ceramic fragmentation, wake hackle pointing the direction of crack propagation from the indentation (pointing finger 1), lateral subsurface crack (pointing finger 2) and the subsurface damage caused by the indentation, which is noticeably more restrained (by the complex microstructure) in D than in C.

Tables:

	VM 7			VM13		
Stressing rate	σ_{water}	$\sigma_{mutans/Rem.}$	σ_i	σ_{water}	$\sigma_{mutans/Rem.}$	σ_i
0.1	25.5 ± 4.8	37.7 ± 9.8	-	42. ± 11.1	44.7 ± 6.6	-
1	33.8 ± 3.6	35.2 ±9.8	-	45.6 ± 10.2	37.1 ± 9.5	-
10	33.2 ± 4,9	34.3 ± 13.1	-	47.1 ± 10.6	46.3 ± 14.1	-
100	36.5 ± 5.9	35 ±11.5	43.9 ± 4.4	47.2 ± 7.2	46.4 ± 16.6	51.53 ± 7.63
n/logϑ_0 (m/s)	27.1/-1	-119.3/-140.3	-	89.4/-0.17	87.9/1.18	-

Table 1. Fracture strength (σ) (Mpa) of VM7 and VM 13 specimens according to the stressing rates. The corresponding fatigue parameters [n/logϑ0 (m/s)], inert strength (σi) (MPa) are also shown.

Figures:

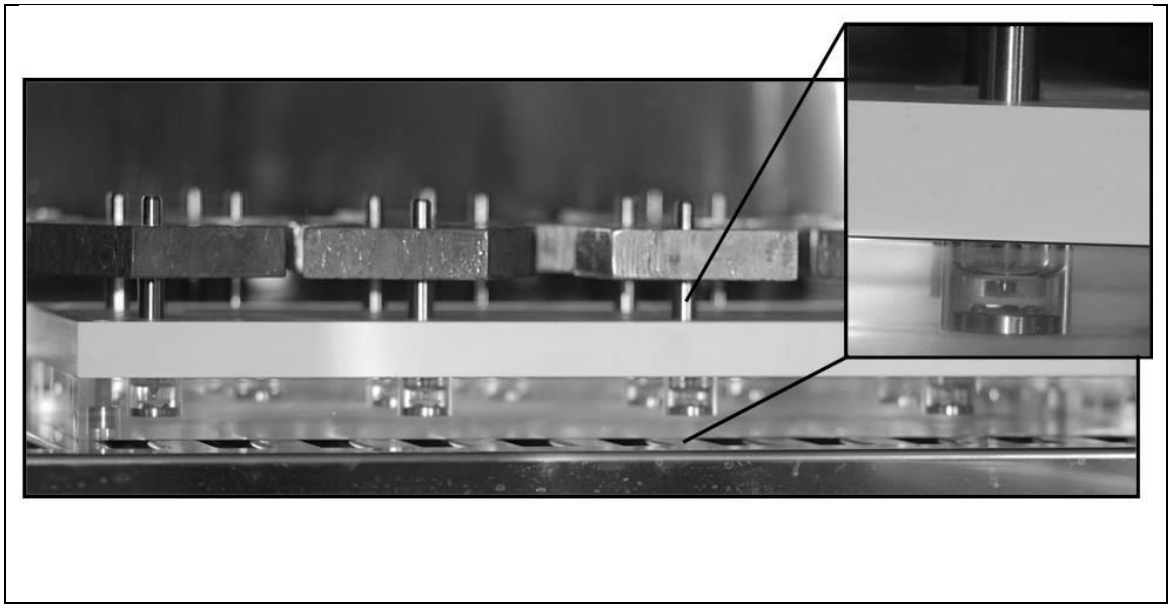

Fig. 1 Adapted plate with dead weights (1 kgf) used for 28-day storage in water or S. mutans/remineralizing solution. The plates also had a 3-stainless-steel-ball base as the biaxial flexure testing device. A piston touched the specimen with a 10 N dead weight.

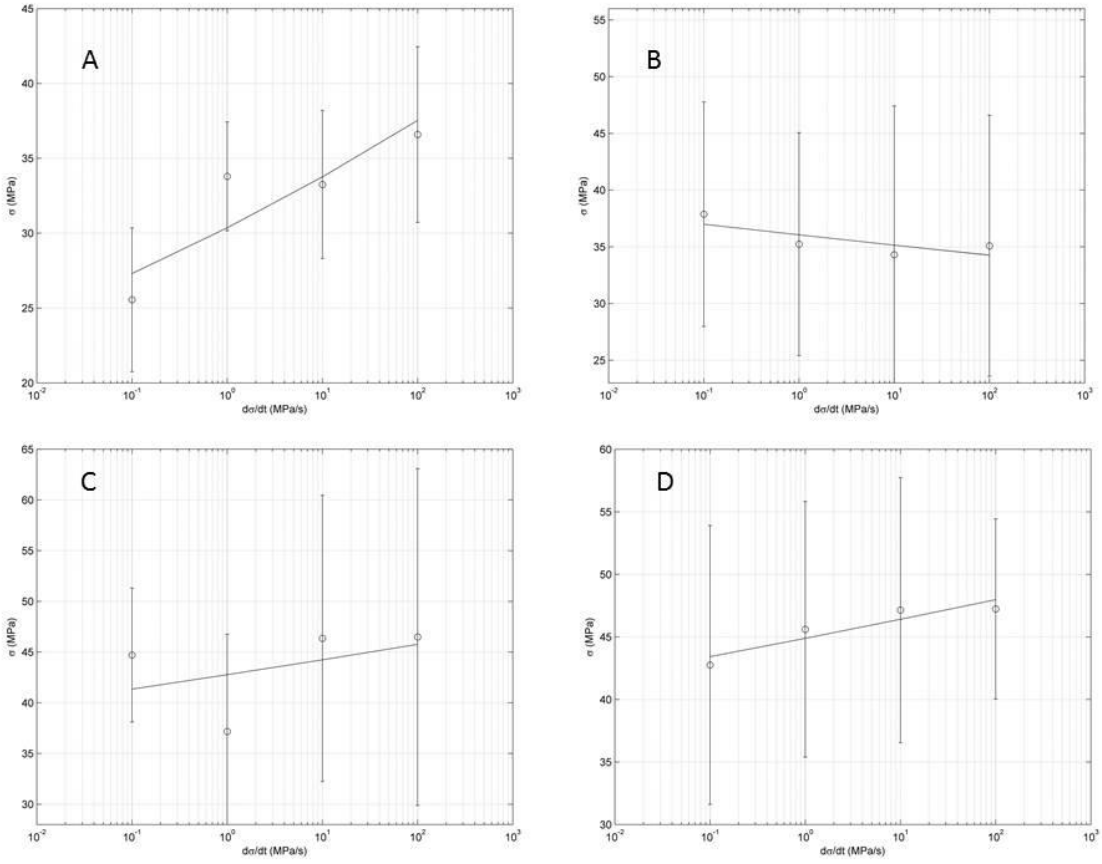

Fig. 2 Plots of strength against the stressing rate of VM 7 (A and B) and VM 13 (C and D) kept in water and *S. mutans*/remineralizing solution, respectively. The exception was VM7 stored in *S. mutans* and remineralizing medium that had a negative "n" value (-119.37) and a complex number for log $\dot{\sigma}_0$. The fatigue parameters of the leucite-reinforced ceramic were higher than those of VM7, no matter the storage medium.

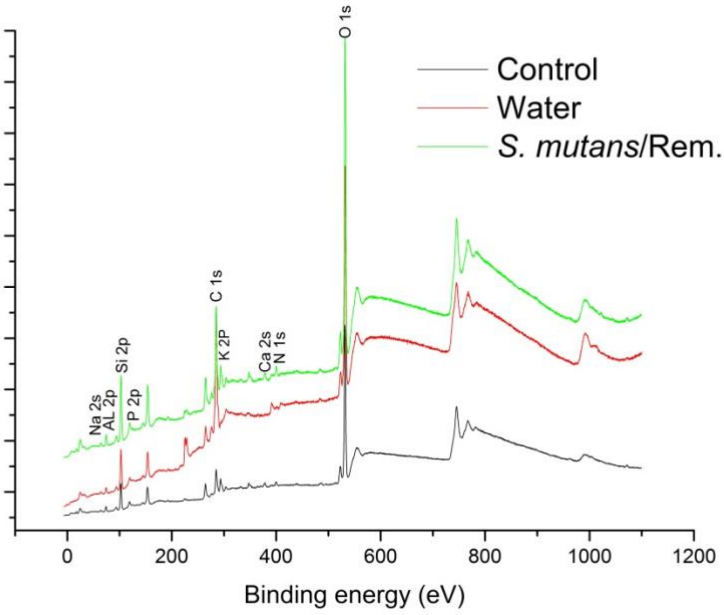

Fig. 3 XPS analyses of VM 7 specimens showing the peaks of the elements present on the ceramic surface of control and experimental groups.

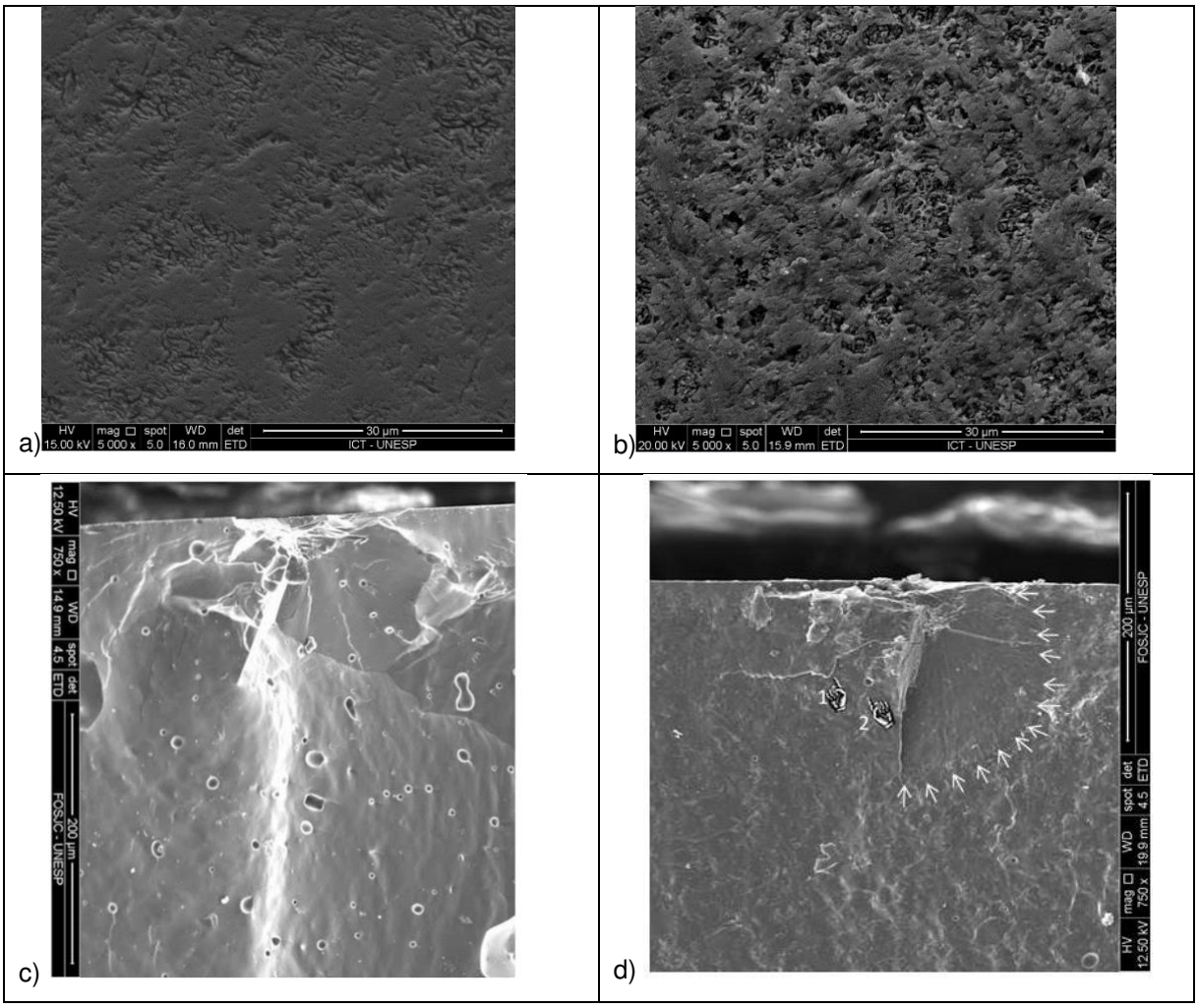

Fig. 4 Acid treated (2 % HF, 20 s) glass and leucite specimens. The empty spaces suggest the crystal morphology ("honeycombs") in B. Specimens fractured at 10 MPa/s after storage in *S mutans*/remineraling medium of Glass (C) and Leucite (D) ceramics. In D, the indentation profile, ceramic fragmentation, wake hackle pointing the direction of crack propagation from the indentation (pointing finger 1), lateral subsurface crack (pointing finger 2) and the subsurface damage caused by the indentation, which is noticeably more restrained (by the complex microstructure) in D than in C.